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A simple technique for producing fullerenes from electrically discharged benzene and toluene

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Abstract : C_{60} and many other fullerenes are found to be present in the electrically discharged benzene and toluene. In the present note we confirm the presence of C_{60} along with other hydrocarbons from the mass spectroscopic studies of the above discharged benzene and toluene products.

Keywords : C_{60}, fullerenes, mass spectroscopy

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It has recently been observed that even numbered clusters of carbon atoms in the range $C_{30} - C_{100}$ are present in carbon vapour [1]. In our earlier communication [2,3], we reported a novel method of producing C_{60} along with other higher and lower fullerenes by electrically discharging pure benzene and toluene. In the present communication, we report the mass spectroscopic data confirming the presence of C_{60} and higher fullerenes along with some polycyclic aromatic hydrocarbons produced upon electric discharge with graphite electrodes in liquid benzene and toluene. Similar results are also obtained with metal electrodes.

We passed ac electric field between two pure graphite electrodes whose pointed tips are immersed in the liquid taken in a double wall quartz beaker with double arms as shown in Figure 1. Cooled water is circulated outside the glass cell. Electric field of the order of 15–20 kV is passed through the electrodes whose pointed tips are already immersed in the liquid. Special care was always taken to avoid accident. Since the electrical contact is made within large amount of benzene or toluene there is little chance of oxidation but several hydrocarbons might produced. As soon as the discharge is started, the liquid tends to become reddish-yellow and then orange-red depending on the magnitude of applied voltage and the time of discharge. The following procedures are adopted for mass spectroscopic analysis :

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(a) Benzene product separation through column chromatography (silica gel) using silica-gel 60 :

The orange-red solution from the cell containing black particles was filtered and the clear orange-red solution was concentrated to 4 ml through evaporation of benzene under vacuum.

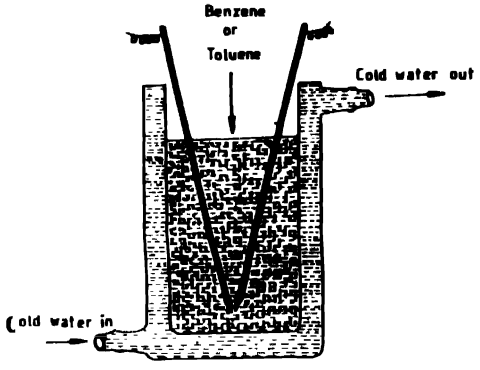

Figure 1 Simple diagram showing the electrical discharge cell along with cooling arrangement

The concentrated solution was then brought at the top of the silica gel column for chromatographic separation of the products. Mixed solvents (benzene : petroleum ether

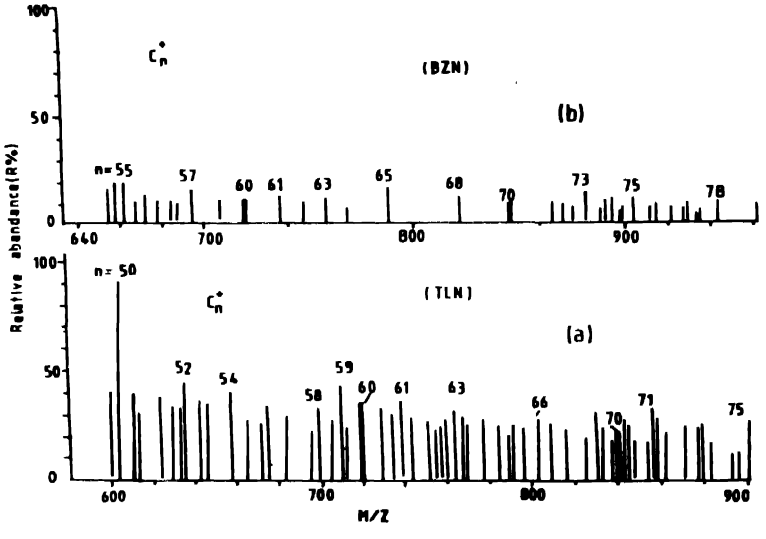

Figure 2. Mass spectroscopic spectra of the toluene (a) and benzene product showing the presence of C_{60} and C_{70} along with other higher fullerenes and hydrocarbons

(40160) = 3 . 1) was used as eluant. A reddish coloured fraction was isolated as the main fraction. Evaporation of benzene under vacuum and washing with ether resulted to the isolation of a red solid (marked as BZN). By increasing the polarity of the solvent upto pure benzene, no further fraction could be isolated.

Plate 1

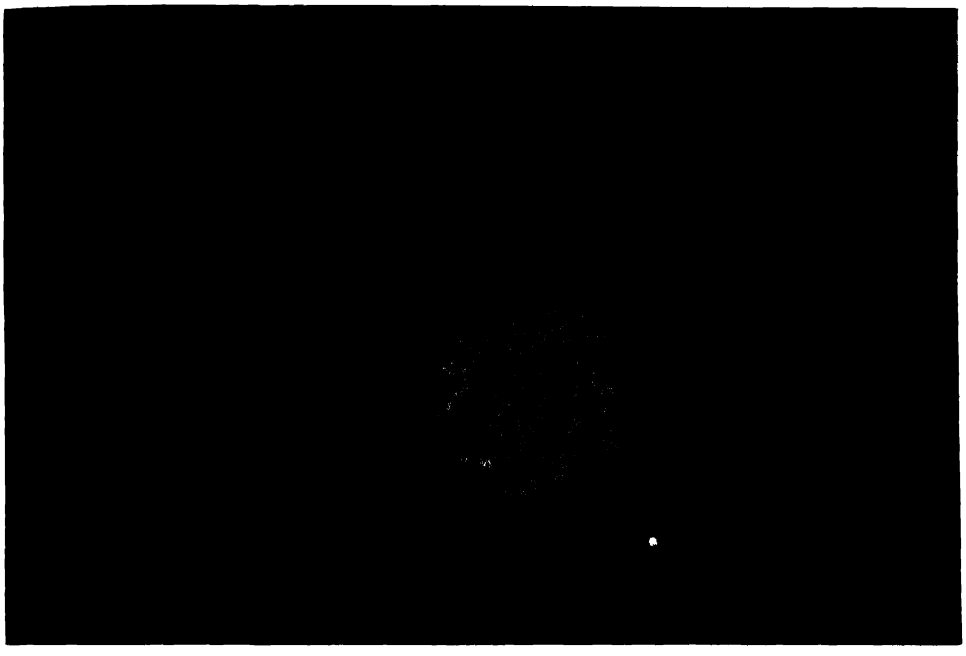

Figure 3(a). Optical spectra of a large single crystal of a fullerene obtained by slow evaporation of the toluence product (magnification 1350 times).

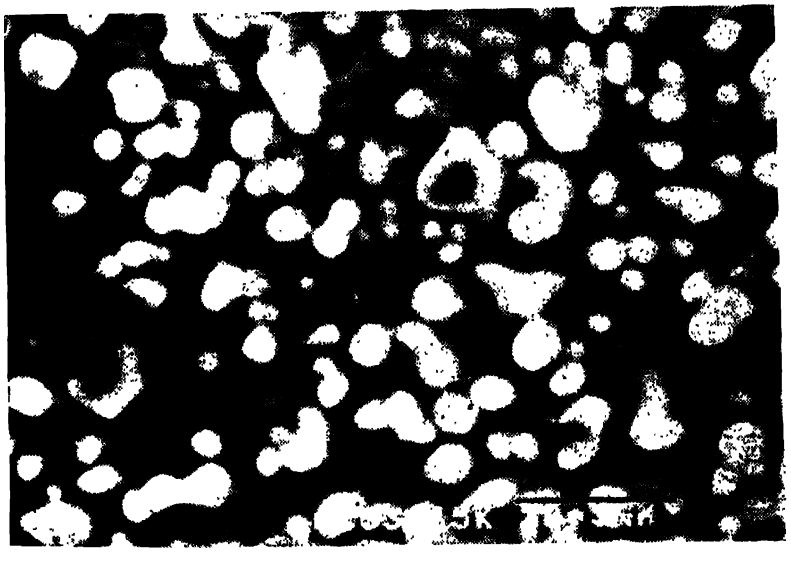

Figure 3(b). Scanning electron micrographs of the thin film of the toluene product (line marked=30 NM).

(b) Toluene product separation through column chromatography (silica gel) using silica gel-60 :

The orange-red coloured solution, from the cell containing black particles was processed similarly as in the case of benzene product discussed above. Mixed solvent (benzene : petroleum ether (40160) = 1 : 1) was used as eluant. Reddish-brown coloured fraction was obtained as the main fraction. Evaporation of toluene under vacuum and washing with ether resulted to the isolation of a red solid (marked as TLN). No further fraction could be obtained.

Both benzene (BZN) and toluene (TLN) products have been analyzed by mass spectroscopy (JEOL-SX-102 (FAB)) and the spectra (Figure 2) showed peaks at 720 a.m.u and 840 a.m.u. along with other fullerenes. As observed from Figure 2 the percentage of C_{60} present in TLN is higher than that present in the BZN product. The higher and lower fullerenes present in the mass spectra are mostly hydrocarbons (C_nH_m). In Table 1 we have listed the M/Z ratio of some of the most probable fullerenes and other hydrocarbons present in the discharged products.

Table 1. The value of M/Z and their relative abundances (R) obtained from mass spectral analysis

Toluene product			Benzene product		
M/Z	Maximum possible carbon atoms C_n^+	R %	M/Z	Maximum possible carbon atoms C_n^+	R %
55	n = 4	66	56	n = 4	76
154	12	53	154	12	45
437	36	48	437	36	13
489	40	52	490	40	10
499	42	48	497	42	11
522	44	54	522	44	13
577	48	52	577	48	47
603	50	100	603	50	100
635	52	46	633	52	16
657	54	43	657	54	18
698	58	36	694	58	17
720	60	35	720	60	12
738	62	38	736	62	14
778	64	30	774	64	10
830	69	34	830	68	10
844	70	32	845	70	12
864	72	25	866	72	12
914	76	34	914	76	13

It is to be mentioned here that the resistivity of the thin films of such red solution is very high (10^{12}–10^{13} ohm-cm at room temperature). Interesting enough to mention that we have been able to isolate a single crystal of a higher fullerene from the slow evaporated red solution of the toluene product as shown in Figure 3a. The icosahedral nature of the crystal is well recognized from this picture. The scanning electron micrograph (SEM) of the film with many small crystals is shown in Figure 3b. The balls are the crystals of fullerenes.

It must finally be concluded that using the present method one could prepare clusters of carbon atoms in the range of C_2–C_{100} or more. Proper conditions for the production and isolation of larger amount of C_{60} molecules are yet to be found. Investigations in this direction are in progress in our laboratory.

Acknowledgment

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References

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[2] **B K Chaudhuri, S Mukherjee and D K Modak 1993 *Proc. Int. Conf. on Fullerenes* (Santa Barbara, California, June 28 –July 1, 1993)**

[3] See also the *Annual Report*, Indian Association for the Cultivation of Science (1991–1992) p 15